Studies on Determinations of Metals by Extraction Method of Metal Organic Compound. III : Determinations of Lead, Silver and Mercury with Sodium Diethyl-dithiocarbamate

Studies on Determinations of Metals by Extraction Method of Metal Organic Compound. III

Determinations of Lead, Silver and Mercury with Sodium Diethyl-dithiocarbamate*

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Synopsis

White precipitates or turbidities of lead, silver and mercury with sodium diethyl-dithiocarbamate were extracted with organic solvents, and their transmittancies were successfully measured at the wave length 340 mμ of Beckman model DU spectrophotometer. By the measurements of the transmittancy of the extracts at the suited wave length, lead as small as 25γ, silver as small as 10γ and mercury as small as 50γ were determinable. Carbon tetrachloride was most useful for the extraction, and benzene, toluene, xylene and chloroform were also useful. The extractions were carried out completely at pH 3~9.5 in lead, pH 2.6~5, in silver and from 3N hydrochloric acid to pH 5.6 in mercury.

I. Introduction

Sodium diethyl-dithiocarbamate (D. C salt) has been mainly used for the microdetermination of copper by many workers(1), that is, the calorimetric measurement on the complex of copper and this reagent were made directly or after extracted with carbon tetrachloride. Concerning other metallic complexes, however, only the obedience of the colorations to Beer's Law was reported, and according to Chernikhow and Dobkina(2), the complex salts of various metals could be extracted with ethylacetate, though the details were unknown. Therefore, it was attempted to determine photometrically the various metal by the relation between the metal content and the extinctancy of the extracts, for the metallic complexes of the organic reagent are extractable with some organic solvents and all give clear extracts, though they are colored or colorless precipitates.

Recently the same experiment was reported on copper, iron, nickel, cobalt, chromium and uranium by R. L. Lacoster, M. H. Earing and S. E. Wiberley(3), in which the extinctancy curve and the suitable wave length of the carbon tetra-

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P. L. Willmot and F. J. Raymond, Analyst, **25** (1950), 24.
(2) Y. A. Chernikhow and B. M. Dobkina, Zavodskaya Lab., **15** (1949), 1148.
(3) R. L. Lacoste, M. H. Earing and S. E. Wiberley, Anal. Chem., **23** (1951), 871.

chloride extracts of those complex salts of metals, the suitable pH range for the extraction and the determinable amount of those metals were studied. Therefore, avoiding the repetition, the present author will report only the experiments on lead, silver and mercury, in which white precipitates were obtained by sodium diethyl-dithiocarbamate, being extractable with organic solvents and which had not yet been studied. The amount of metal and the extinctancy of the extract measured respectively at the suitable wave length by means of the Beckman model DU spectrophotometer were each in a linear relation, which was applicable for the determination of each metal. The suitable organic solvent for the extraction and the pH range required in the procedure were determined.

II. Experimental results

(1) Instrument and reagents

The extinctancy was measured in a 1 cm cell of the Beckmann model DU spectrophotometer. The measurement of pH was made by means of a hydrogen electrode. The reagent was 0.1 per cent sodium diethyl-dithiocarbamate solution (0.1 per cent D. C. sodium salt solution). The buffer solutions used were 0.2 M acetic acid, 0.2 M sodium acetate, 0.2 M ammonium acetate, ammonium hydroxide, 0.2 M sodium hydroxide, 0.2 M hydrochloric acid and 0.2 M potassium chloride solutions. The organic solvents used were carbon tetrachloride chloroform, toluene, xylene and others. The standard solutions of metals were prepared respectively as follows: the lead standard solution (100 γ/ml) was prepared from lead nitrate of "extra pure" grade and standarized gravimetrically by the lead sulfate method; the silver standard solution (100 γ/ml) was prepared from silver nitrate of "extra pure" grade and standarized gravimetrically by the silver chloride method; the mercury standard solution (200 γ/ml) was prepared from mercuric chloride of "extra pure" grade and standarized by the electrolytic method.

(2) Measurement

10 ml of pH 3.7 buffer solution and 2 ml of 0.1 per cent D. C. salt solution were added to the metal solution and thus obtained metallic complex was extracted with the organic solvent. The absorbancy curve of the extract was measured by the photometer and the most suitable wave length thus obtained was employed for the extinctancy measurement in the determination of the metal.

(3) Absorbancy curve

The complexes of various metals with the D. C. salt were extracted with carbon tetrachloride and the transmittancy of the extracts was measured respectively at wave lengths of 320~1000 mμ. By the transmittancy measured the absorbancy curves were drawn.

(4) Experimental procedure

Taking 1 ml of each metal standard solution and 10 ml of the buffer solution of pH 3.7 in to a separating funnel, 2 ml of D. C. salt solution and 5 ml of carbon tetrachloride were added to it, and the funnel was shaked vigorously for one minute. After it was settled the carbon tetrachloride phase was drawn off from

the aqueous phase and the transmittancy of the extract was measured in 1 cm cell at wave lengths of 320~1000 mμ. The blanks were obtained by treating the solution in the same way as above in which only the metal solution was not contained. The absorbancy curve of the various metals are shown in Fig. 1. It was found from the result that the wave length of 340mμ was most suitable for the measurement. More intensive absorptions were shown at 320 mμ, but an absorption of the reagent itself was large through the ultraviolet ray shorter than 330 mμ and greatly decreased through the ray longer than 340mμ. Extinctancy of the reagent itself is shown in Fig. 2.

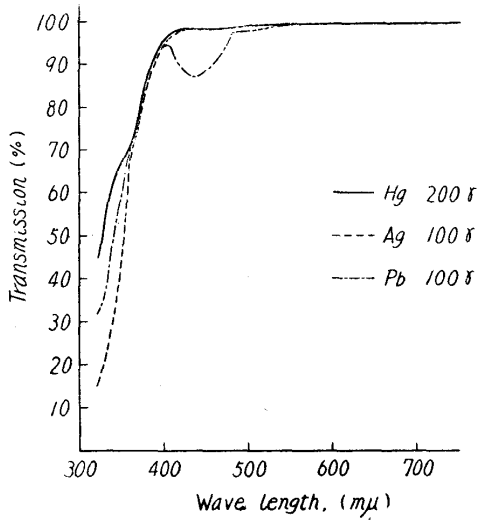

Fig. 1

(5) Influence of pH

Preparing various kinds of buffer solutions of pH, the suitable pH range for the extraction was studied. Carbon tetrachloride was used as an extracting solvent in this experiment.

Treating as described above, the extract was measured at the most suitable wave length of 340 mμ. The results obtained by this experiment are shown in Fig. 3. As shown in Fig. 3, the extraction of lead was complete at pH 3~9.5 and uncomplete at a lower pH than 3; that of silver was complete at pH 2.6~5, and gave somewhat low but definite values at pH 6~9.5 and was uncomplete at a higher pH than 9.5; that of mercury was complete at a lower pH than 5.6 from 3N of hydrochloric acid and gave somewhat low values until pH 9.5.

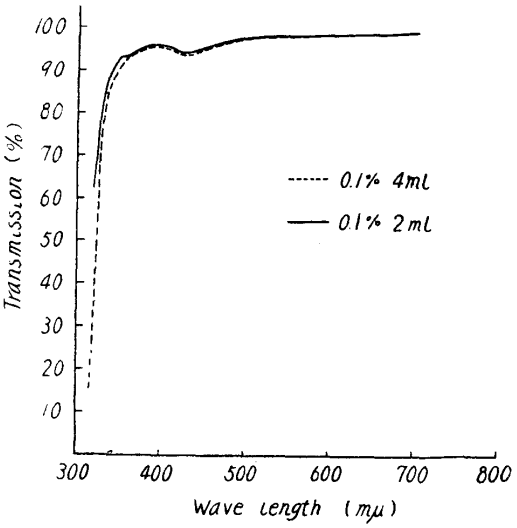

Fig. 2

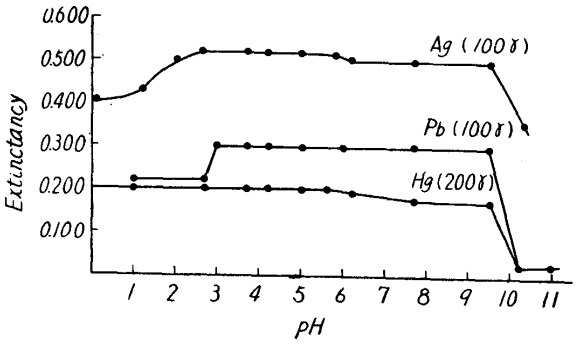

Fig. 3

(6) Relation between the amount of metal and the extinctancy

The solutions of pH 3.7 containing various amounts of the metal were treated and their extinctancy were measured. The results obtained are shown in Fig. 4.

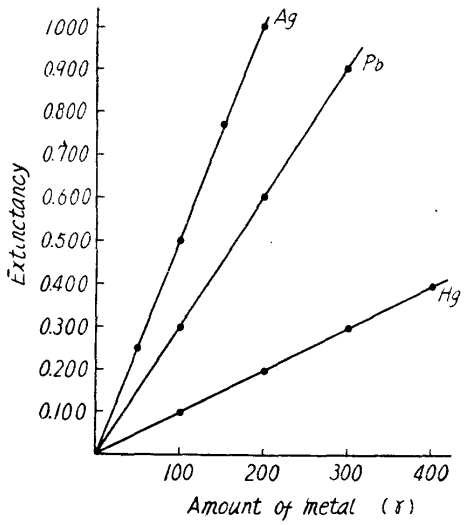

Fig. 4

As shown in Fig. 4, linear relations were obtained, by which lead of 25~300 γ, silver of 10~200 γ and mercury of 50~400 γ were determinable.

(7) Solvents

The extractabilities of various kinds of solvents were compared.

(i) Lead

The extraction was carried out with 5ml of carbon tetrachloride, amylalcohol, amylacetate, toluene, xylene, benzene and chloroform, and the extinctancy of the extract was measured as shown in Table 1. There was no large difference in these solvents, but carbon tetrachloride was the best, and xylene, toluene, benzene and amylacetate were almost of the same degree.

Table 1

Solvents	Extinctancy (E)		
	Amount of Lead (γ)		
	100	150	200
Carbon tetrachloride	0.300	0.450	0.600
Amylacetate	0.270	0.400	0.530
Xylene	0.285	0.417	0.568
Toluene	0.275	0.420	0.566
Chloroform	0.270	0.430	0.555
Benzene	0.270	0.425	0.568

340 mμ pH 3.7

Amylalcohol gave rather low and different values with different pH, and had a poor reproducibility and a tendency to produce some turbidity at a higher pH than 7.8.

The extraction of the solution containing 100γ of lead was complete by once with 5 ml of carbon tetrachloride and the second extract gave no absorption.

(ii) Silver

Carbon tetrachloride was the best, and benzene toluene, xylene and chloroform gave a rather low but simillar values, and amylacetate and amylalcohol gave some turbidity.

(iii) Mercury

When 200γ of mercury was extracted at pH 3.7, chloroform, benzene, toluene, xylene and amylacetate gave the same degree of absorption, but gave somewhat lower value than that of carbon tetrachloride which gave the largest extinctancy.

III. Consideration

Determinations of metals had already been carried out on the basis of the

coloration of the metal complexes with sodium diethyl-dithiocarbamate or on that of the coloration of the extracts of the metal complexes with an organic solvent, whereas lead, silver and mercury formed some white precipitates or turbidities with the reagent and their extraction with an organic solvent had been used only for the separation. According to the experimental results by the present author, the precipitates or the turbidities of the metal complexes with the reagent were all completely extractable in a definite pH range with some organic solvents. From the extract the determination of the metals could be carried out photometrically, for the most suitable absorption of the extract was obtained through 340 mμ in the ultraviolet part using the Beckman model DU spectrophotometer, and its extinctancy measured through the ray was linear against the amount of the metals. The suitable pH range were also found in which the extractions were carried out completely. It was found that lead as little as 25γ, silver as little as 10γ and mercury as little as 50γ were determinable by this procedure.

Summary

(1) Silver, mercury and lead formed some white precipitates or turbidities with sodium diethyl-dithiocarbamate, and the complexes of a white precipitate or a turbidity were extractable with some organic solvents giving some transparent extracts.

(2) According to the absorbancy curve of the extract drawn after the transmittancy measurements by means of the Beckman model DU spectrophotometer, the most suitable wave length for the determinations was 340 mμ.

(3) The extinctancy measured through the suitable wave length was linear against the amount of the metal. Silver as small as 10γ, lead as small as 25γ and mercury as small as 50γ were determinable by this procedure.

(4) The best extracting solvents was carbon tetrachloride. Benzene, toluene, xylene and chloroform were also useful giving almost the same degree of an absorption, though somewhat low value. Amylalcohol and amylacetate seemed to be not suitable owing to a formation of some turbidity.

(5) Suitable pH range for the extraction was 2.6~5 in silver, 3~9.5 in lead and from 3N of hydrochloric acid to pH 5.6 in mercury.

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